



# **CHE 425**

# **Engineering Economics and Design Principles**



# **CHAPTER 4**

## **Understanding Process Conditions**



**The ability to make an economic analysis of a chemical process based on a PFD is not proof that the process will actually work.**



## PURPOSE OF CHAPTER 4

- ❑ Analyze reasons for selecting specific conditions:
  - Temperatures
  - Pressures
  - Compositions
- ❑ Analyze process conditions that require special consideration



## CONDITIONS OF SPECIAL CONCERN

- ❑ It is easier to adjust T and/or P of a stream than to change composition.
- ❑ The following conditions do not cause severe difficulties
  - Temperatures between 40 - 260 C
  - Pressures between 1 - 10 bar
- ❑ Conditions outside the above favored temperature and pressure ranges are identified as “conditions of special concern”



# PRESSURE

Above 10 bar

- Thicker walled expensive equipment
- Safety issue

1- 10 bar

- Favorable condition

Below 1 bar

- Large equipment
- Special construction material

Increase in cost



## **PRESSURE (cont.)**

**A decision to operate outside  
the pressure range of 1-10  
bar must be justified**

## TEMPERATURE (cont.)

### Example 4.1

The maximum allowable tensile strength for a typical carbon steel and stainless steel, at ambient temperature, 400°C, and 550°C is provided below (from Walas [1]).

Temperature	Tensile Strength of Material at Temperature Indicated (bar)		
	Ambient	400°C	550°C
Carbon Steel (grade 70)	1190	970	170
Stainless Steel (Type 302)	1290	1290	430

Determine the fractional decrease in the maximum allowable tensile strength (relative to the strength at ambient conditions) for the temperature intervals: (a) ambient to 400°C and (b) 400°C to 550°C.





## TEMPERATURE (cont.)

a. Interval: ambient to 400°C:

$$\text{Carbon Steel: } (1190-970)/1190 = 0.18$$

$$\text{Stainless Steel: } (1290-1290)/1290 = 0.0$$

b. Interval: 400°C to 550°C:

$$\text{Carbon Steel: } (970-170)/1190 = 0.67$$

$$\text{Stainless Steel: } (1290-430)/1290 = 0.67$$

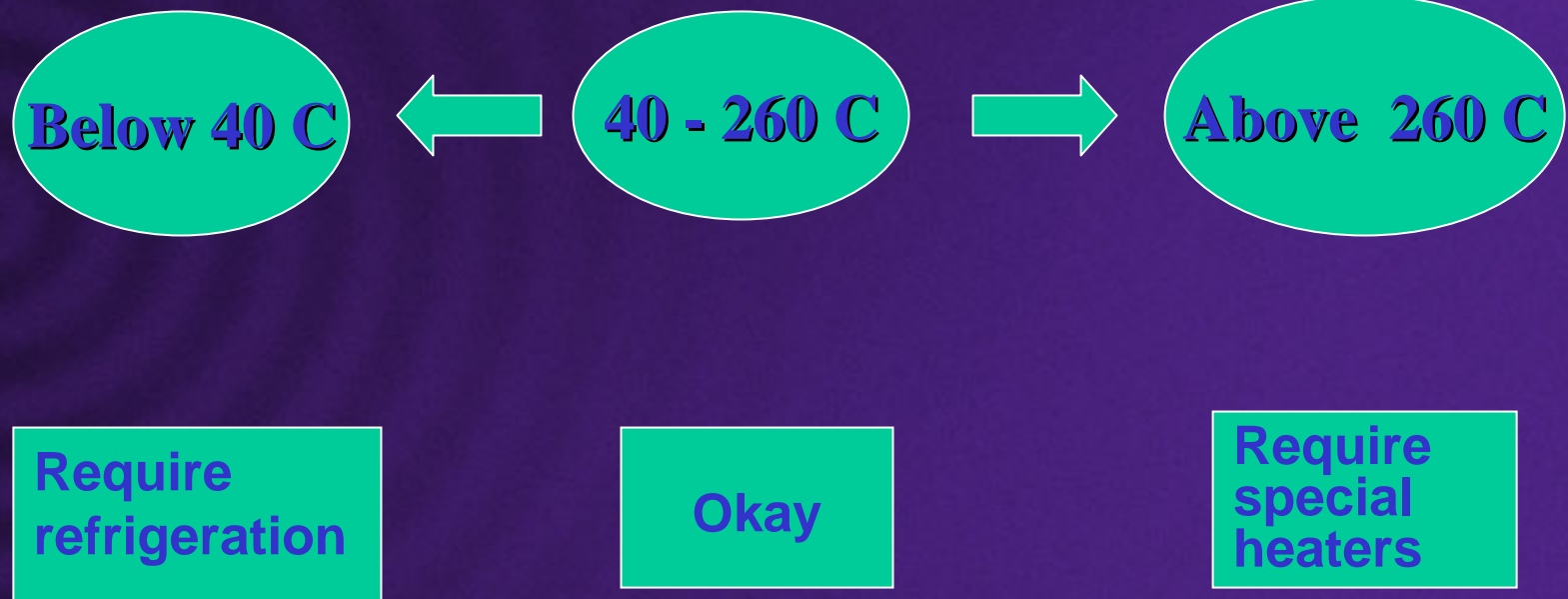


## **TEMPERATURE (cont.)**

**A decision to operate above  
400 C must be justified**



## TEMPERATURE (cont.)



## TEMPERATURE (cont.)

- $T < 40^{\circ}\text{C}$  – Refrigeration
  - ◆ Use as much Cooling Water as Possible



- ◆ Operating Costs (Table 3.4)
  - ◆ Cooling Water \$0.16/ GJ
  - ◆ Refrigerated Water \$20.60/ GJ



## Do we ever operate outside these limits?

- Tables 4.1 – 4.3
  - ◆ Reactors and Separators
- Table 4.4
  - ◆ Other Equipment
- DME Process – pretty much inside limits



## REASONS FOR OPERATING AT CONDITIONS OF SPECIAL CONCERN

- ① Favorable equilibrium conversion
- ② Increase in reaction rates

$$k_{reaction} = k_0 e^{-\frac{E_{act}}{RT}}$$

- ③ Maintain a gas phase
- ④ Improve selectivity



## Table 4.1

**Table 4.1 Possible Reasons for Operating Reactors and Separators Outside the Temperature Ranges of Special Concern**

Stream Condition	Process Justification for Operating at This Condition	Penalty for Operating at This Condition
High Temperature [ $T > 250^{\circ}\text{C}$ ]	<p><b>REACTORS</b></p> <ul style="list-style-type: none"> <li>(i) Favorable equilibrium conversion for endothermic reactions</li> <li>(ii) Increase reaction rates</li> <li>(iii) Maintain a gas phase</li> <li>(iv) Improve selectivity</li> <li>(v)</li> <li>(vi)</li> </ul> <p><b>SEPARATORS</b></p> <ul style="list-style-type: none"> <li>(i) Obtain a gas phase required for vapor-liquid equilibrium</li> <li>(ii)</li> <li>(iii)</li> </ul>	<ul style="list-style-type: none"> <li>i) Use of special process heaters</li> <li>(ii) <math>T &gt; 400^{\circ}\text{C}</math> requires special materials of construction</li> <li>(iii)</li> <li>(iv)</li> <li>(v)</li> </ul>



**Table 4.1 (cont.)**

Low  
Temperature  
[ $T < 40^{\circ}\text{C}$ ]

**REACTORS**

- |   |  |
|---|--|
| <ul style="list-style-type: none"> <li>(i) Favorable equilibrium conversion for exothermic reactions</li> <li>(ii) Temperature sensitive materials</li> <li>(iii) Improve selectivity</li> <li>(iv) Maintain a liquid phase</li> <li>(v)</li> <li>(vi)</li> </ul> | <ul style="list-style-type: none"> <li>(i) Uses expensive refrigerant</li> <li>(ii) May require special materials of construction for very low temperatures</li> <li>(iii)</li> <li>(iv)</li> <li>(v)</li> </ul> |
|---|--|

**SEPARATORS**

- (i) Obtain a liquid phase required for vapor-liquid or liquid-liquid equilibrium
- (ii) Obtain a solid phase for crystallization
- (iii) Temperature sensitive materials
- (iv)
- (v)





**Table 4.2**

**Table 4.2 Possible Reasons for Operating Reactors and Separators Outside the Pressure Range of Special Concern**

Stream Condition	Process Justification for Operating at This Condition	Penalty for Operating at This Condition
High Pressure ( $P > 10$ bar)	<p><b>REACTORS</b></p> <ul style="list-style-type: none"> <li>(i) Favorable equilibrium conversion</li> <li>(ii) Increase reaction rates for gas phase reactions (due to higher concentration)</li> <li>(iii) Maintain a liquid phase</li> <li>(iv)</li> <li>(v)</li> </ul>	<ul style="list-style-type: none"> <li>(i) Requires thicker-walled equipment</li> <li>(ii) Requires expensive compressors if gas streams must be compressed</li> <li>(iii)</li> <li>(iv)</li> <li>(v)</li> </ul>
	<p><b>SEPARATORS</b></p> <ul style="list-style-type: none"> <li>(i) Obtain a liquid phase for vapor-liquid or liquid-liquid equilibrium</li> <li>(ii)</li> <li>(iii)</li> </ul>	



## Table 4.2 (cont.)

Low  
Pressure  
( $P < 1$  bar)

### REACTORS

- (i) Favorable equilibrium conversion
- (ii) Maintain a gas phase
- (iii)
- (iv)

- (i) Requires large equipment
- (ii) Special design for vacuum operation
- (iii) Air leaks into equipment that may be dangerous and expensive to prevent
- (iv)
- (v)
- (vi)

### SEPARATORS

- (i) Obtain a gas phase for vapor-liquid equilibrium
- (ii) Temperature-sensitive materials
- (iii)
- (iv)



**Table 4.3**

**Table 4.3 Possible Reasons for Nonstoichiometric Reactor Feed Compositions of Special Concern**

Stream Condition	Process Justification for Operating at This Condition	Penalty for Operating at This Condition
Inert Material in Feed to Reactor	<ul style="list-style-type: none"> <li>(i) Acts as a diluent to control the rate of reaction and/or to ensure that the reaction mixture is outside the explosive limits (exothermic reactions)</li> <li>(ii) Inhibits unwanted side reactions</li> <li>(iii)</li> <li>(iv)</li> </ul>	<ul style="list-style-type: none"> <li>(i) Causes reactor and downstream equipment to be larger since inert takes up space</li> <li>(ii) Requires separation equipment to remove inert material</li> <li>(iii) May cause side reactions (material is no longer inert)</li> <li>(iv) Decreases equilibrium conversion</li> <li>(v)</li> <li>(vi)</li> </ul>
Excess Reactant	<ul style="list-style-type: none"> <li>(i) Increases the equilibrium conversion of the limiting reactant.</li> <li>(ii) Inhibits unwanted side reactions.</li> <li>(iii)</li> <li>(iv)</li> </ul>	<ul style="list-style-type: none"> <li>(i) Requires separation equipment to remove excess reactant</li> <li>(ii) Requires recycle</li> <li>(iii) Added feed material costs (due to losses in separation and/or no recycle)</li> <li>(iv)</li> <li>(v)</li> </ul>



**Table 4.3 (cont.)**

<p>Product present in feed to reactor</p>	<ul style="list-style-type: none"> <li>(i) Product cannot easily be separated from recycled feed material.</li> <li>(ii) Recycled product retards the formation of unwanted by-products formed from side reactions.</li> <li>(iii) Product acts as a diluent to control the rate of reaction and/or to ensure that the reaction mixture is outside the explosive limits, for exothermic reactions.</li> </ul>	<ul style="list-style-type: none"> <li>(i) Causes reactor and downstream equipment to be larger</li> <li>(ii) Requires larger recycle loop</li> <li>(iii) Decreases equilibrium conversion</li> <li>(iv)</li> <li>(v)</li> </ul>
<ul style="list-style-type: none"> <li>(iv)</li> <li>(v)</li> </ul>		



## Table 4.4

**Table 4.4 Changes in Process Conditions That Are of Special Concern for a Stream Passing through a Single Piece of Equipment**

Type of Equipment	Change in Stream Condition Causing Concern	Justification or Remedy	Penalty for Operating Equipment in this Manner
1. Compressors	$P_{out}/P_{in} > 3$	<b>Remedy:</b> Use multiple stages and intercoolers	High theoretical work requirement due to large temperature rise of gas stream
	High temperature inlet gas	<b>Remedy:</b> Cool the gas before compression.	High theoretical work requirement and special construction materials required
2. Heat Exchangers	$\Delta T_{lm} > 100^{\circ}\text{C}$	<b>Remedy:</b> Integrate heat better within process (see Chapter 13)  <b>Justification:</b> Heat integration not possible or not profitable	Large temperature driving force means we are wasting valuable high-temperature energy



**Table 4.4 (cont.)**

3. Process  
Heaters

$$T_{out} < T_{steam\ available}$$

**Remedy:** Use high-pressure steam to heat process stream

Process heaters are expensive and unnecessary if heating may be accomplished by using an available utility

**Justification:** Heater may be needed during start-up

4. Valves

Large  $\Delta P$  across valve

**Remedy:** For gas streams install a turbine to recover lost work

Wasteful expenditure of energy due to throttling

**Justification:**

- (a) Valve used for control purposes
- (b) Installation of turbine not profitable
- (c) Liquid is being throttled



**Table 4.4 (cont.)**

5. Mixers (streams mixing)	Streams of greatly differing tempera- tures mix	<b>Remedy:</b> Bring temperatures of streams closer together using heat integration	Wasteful expenditure of high-temperature energy
	Streams of greatly differing composi- tion mix	<b>Justification:</b> (a) Quenching of reaction products (b) Provides driving force for mass transfer	Causes extra separation equipment and cost

## Example 4.2

### Example 4.2

It is necessary to provide a nitrogen stream at 80°C and a pressure of 6 bar. The source of the nitrogen is at 200°C and 1.2 bar. Determine the work and cooling duty required for three alternatives.

- Compress in a single compression stage and cool the compressed gas.
- Cool the feed gas to 80°C and then repeat Part a, above.
- Repeat Part b, above, except use two stages of compression with an intercooler.
- Identify any conditions of special concern that occur.

Nitrogen can be treated as an ideal diatomic gas for this comparison. Use as a basis 1 kmol of nitrogen and assume that the efficiency,  $\epsilon$ , of each stage of compression is 70%.

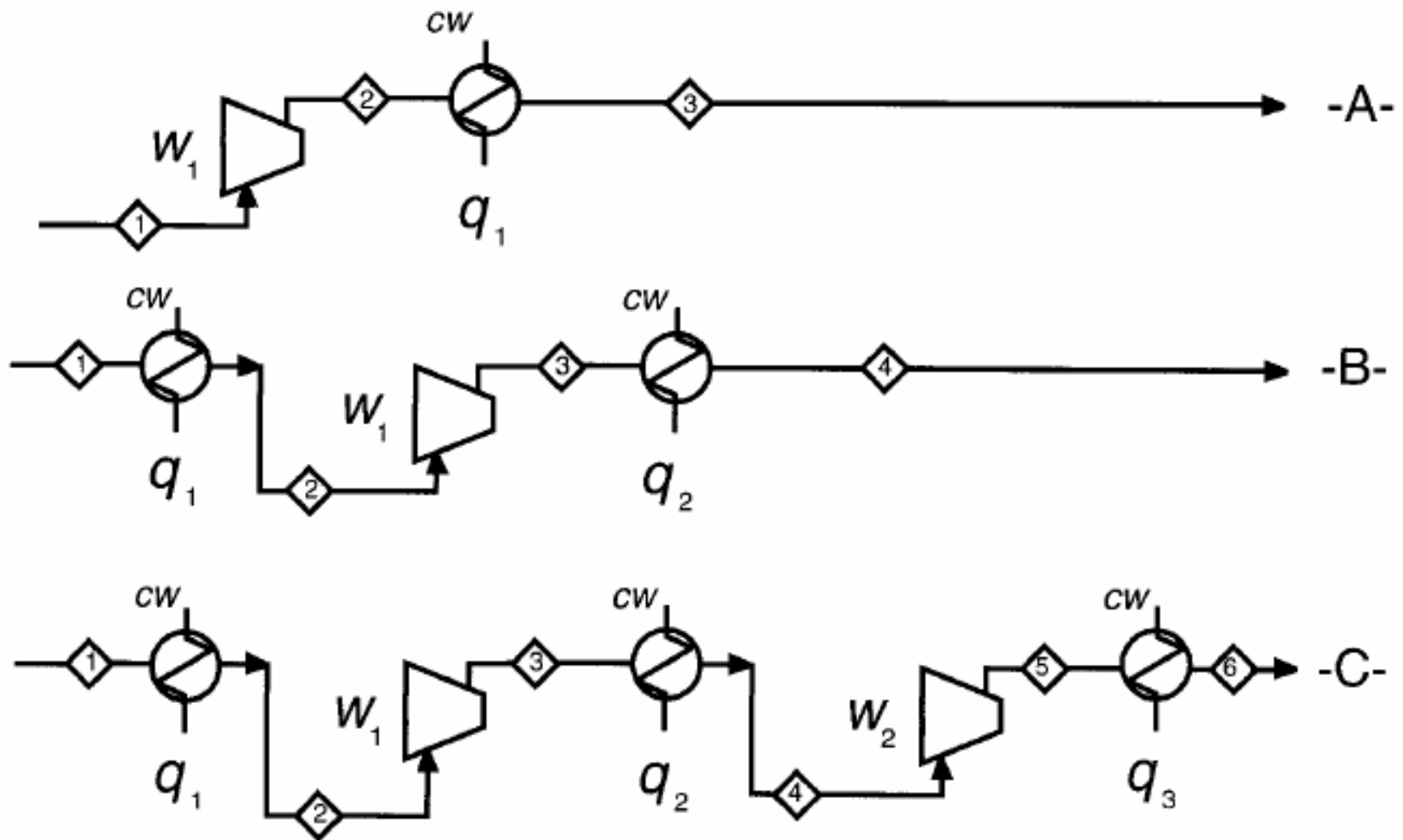
For ideal diatomic gas:  $C_p = 3.5R$ ,  $C_v = 2.5R$ ,  $\gamma = C_p/C_v = 1.4$ ,  $R = 8.314 \text{ kJ/kmol K}$ ,  
 $\epsilon = 0.70$

Equations used:  $q = C_p\Delta T$ ,  $w = RT_{in}\gamma/(\gamma-1)[(P_{out}/P_{in})^{(\gamma-1)/\gamma} - 1]/\epsilon$ ,

$$T_{out} = T_{in}(1 + 1/\epsilon)[(P_{out}/P_{in})^{(\gamma-1)/\gamma} - 1]$$



## Example 4.2 (cont.)

**Figure E4.2** Alternative Process Schemes for Compression of Nitrogen



## Example 4.2 (cont.)

**Table E4.2 Flow Summary Table for Example 4.2 and Figure E4.2**

Stream No. in Figure E4.2	System -A-		System -B-		System -C-	
	$T(^{\circ}\text{C})$	$P(\text{bar})$	$T(^{\circ}\text{C})$	$P(\text{bar})$	$T(^{\circ}\text{C})$	$P(\text{bar})$
1	200	1.2	200	1.2	200	1.2
2	595	6.0	80	1.2	80	1.2
3	80	6.0	374	6.0	210	2.68
4	—	—	80	6.0	80	2.68
5	—	—	—	—	210	6.0
6	—	—	—	—	80	6.0
<b>Work: kJ/kmol</b>						
$w_1$	11,470		8560		3780	
$w_2$	—		—		3780	
$w_{total}$	11,470		8560		7560	
<b>Heat: kJ/kmol</b>						
$q_1$	14,970		3490		3490	
$q_2$	—		8550		3780	
$q_3$	—		—		3780	
$q_{total}$	14,970		12,040		11,050	



## Example 4.2 (cont.)

Figure E4.2 gives the process flow diagrams for the three alternatives and identifies stream numbers and utilities.

The results of the calculations for Parts a, b, and c are provided in Table E4.2, which shows stream conditions and utility requirements. To keep the calculations simple, the pressure drops across and between equipment have been ignored.

Part d: Alternative -A- requires a compressor exit temperature of  $595^{\circ}\text{C}$  that is a condition of special concern. Note also that although the intermediate temperature of the gas (stream) in Alternative -B- was  $374^{\circ}\text{C}$ , because this stream is to be cooled there are no concerns about utility requirements.



## Process Conditions Matrix (PCM)

Table 4.5 Process Conditions Matrix for the PFD of the Toluene Hydrodealkylation Process Shown in Figure 1.5

Equipment	Reactors and Separators Tables 4.1–4.3					Other Equipment Table 4.4				
	High Temp	Low Temp	High Pres.	Low Pres.	Non-Stoich. Feed	Comp	Exch.	Htr.	Valve	Mix
R-101	X		X		X					
V-101										
V-102			X							
V-103										
V-104										
T-101										
H-101										
E-101							X			
E-102							X			





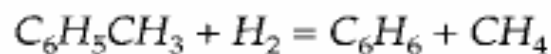
## Evaluation of Reactor R-101

- Three conditions of concern
  - ◆ High Temperature
  - ◆ High Pressure
  - ◆ Non-stoichiometric Feed Conditions

## Additional Information about toluene HDA reaction

**Table 4.6 Equilibrium and Reaction Kinetics Data for the Toluene Hydrodealkylation Process**

### Reaction Stoichiometry



toluene

benzene

### Equilibrium Constant ( $T$ is in units of K)

$$\ln(K_p) = 13.51 + \frac{5037}{T} - 2.073\ln(T) + 3.499 \times 10^{-4}T + 4.173 \times 10^{-8}T^2 + \frac{3017}{T^2}$$

### Heat of Reaction

$$\Delta H_{reaction} = -37,190 - 17.24T + 29.09 \times 10^{-4}T^2 + 0.6939 \times 10^{-6}T^3 + \frac{50,160}{T} \quad \frac{\text{kJ}}{\text{kmol}}$$

**At the Reaction Conditions of 600°C (873 K)**

Equilibrium Constant,  $K_p = 265$

Heat of Reaction,  $\Delta H_{reaction} = -49,500 \quad \frac{\text{kJ}}{\text{kmol}}$

### Information on Reaction Kinetics

No side reactions

Reaction is kinetically controlled

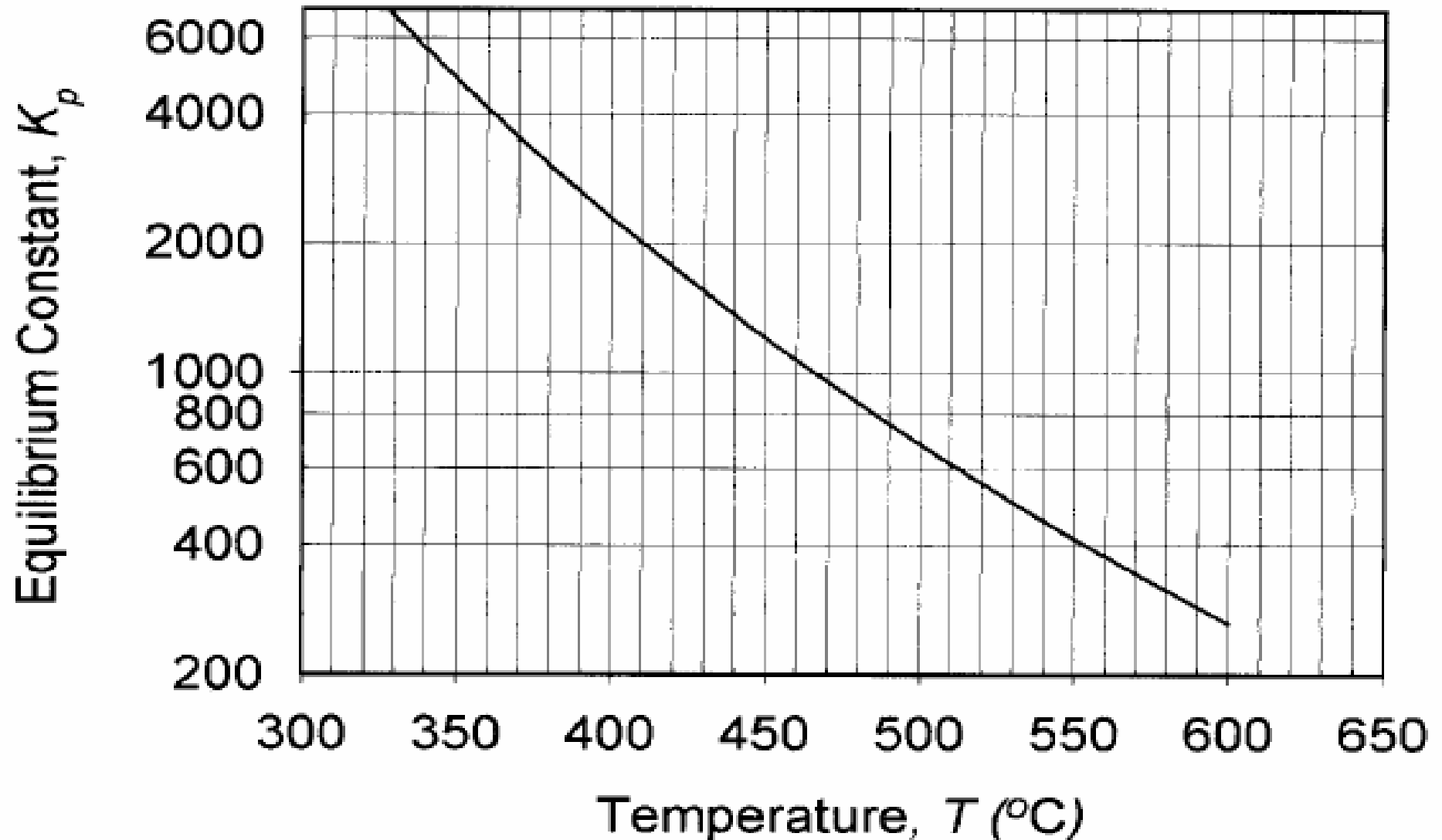


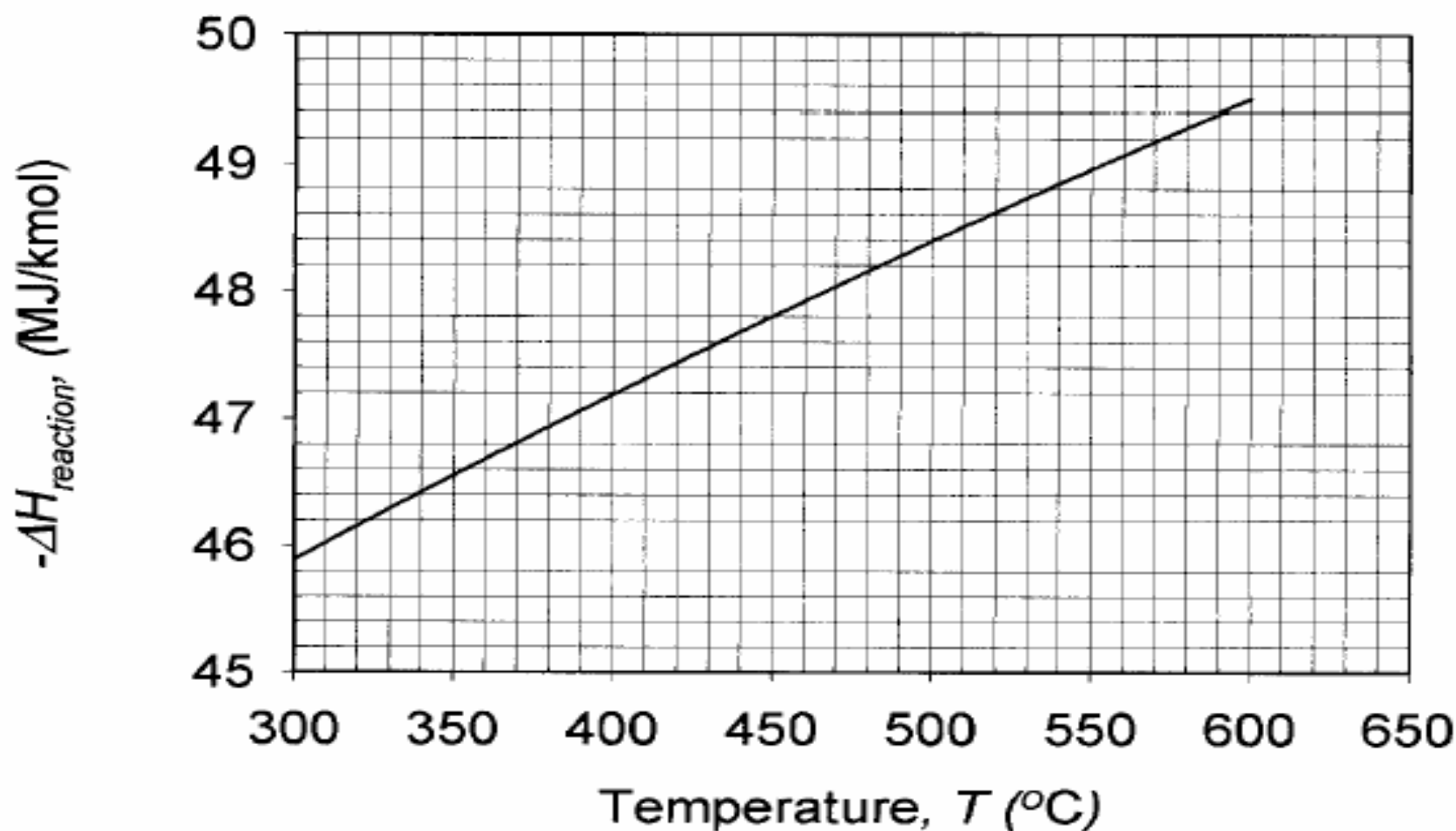
## Reactor Analysis

The analysis of the reactor takes place in two parts.

- a. Evaluation of the special conditions from the thermodynamic point of view. This assumes that chemical equilibrium is reached and provides a limiting case.
- b. Evaluation of the special conditions from the kinetics point of view. This accounts for the limitations imposed by reaction kinetics, mass transfer, and heat transfer.







**Figure 4.1** Equilibrium Constant and Heat of Reaction as a Function of Temperature for the Toluene Hydrodealkylation Reaction



# Thermodynamic Consideration

- High temperature concern
  - ◆ Fig 4.1 implies the rxn is exothermic
  - ◆ For exothermic rxn, as  $T \uparrow$ ,  $X_{eq} \downarrow$
  - ◆ Decrease in  $X_{eq}$  is undesirable
  - ◆ Use of high  $T$  cannot be justified from thermodynamic point of view



## Thermodynamic Consideration (cont.)

- High pressure concern
  - ◆ Rxn stoichiometry shows that there are equal number of reactant and product moles in the HDA rxn.
  - ◆ Thus, no effect of pressure on  $X_{eq}$
  - ◆ No reason to use high P from thermodynamic point of view

## Example 4.3

### Example 4.3

For the PFD presented in Figure 1.5:

- Calculate the actual conversion
- Evaluate the equilibrium conversion at 600°C.

Assuming ideal gas behavior:  $K_p = (N_{benzene} N_{methane}) / (N_{toluene} N_{hydrogen})$

where  $N$  represents the moles of each species at equilibrium

Information on the feed stream to the reactor from Table 1.5 (Stream 6 on Figure 1.5).

Hydrogen	735.4 kmol/h
Methane	317.3
Benzene	7.6
Toluene	144.0
Total	1204.3



### Example 4.3 (cont.)

- a. Actual Conversion: Toluene in exit stream (Stream 9) = 36 kmol/h

$$\text{Conversion} = (144 - 36)/144 = 0.75 \text{ (75\%)}$$

- b. Equilibrium Conversion at 600°C. From Table 8.6 @600°C  $K_p = 265$

Let  $N =$  kmol/h of benzene formed

$$265 = [(N + 7.6)(N + 317.3)]/[(735.4 - N)(144 - N)]$$

$$N = 143.5$$

$$\text{Equilibrium Conversion} = 143.6/144 = 0.997 \text{ (99.7\%)}$$



## Example 4.4

### Example 4.4

(Reference Example 4.3) Reduce the amount of hydrogen in the feed to the reactor to the stoichiometric amount, that is, 144 kmol/h, and determine the effect on the equilibrium conversion at 600°C.

The calculations are not shown. They are similar to those in Example 4.3(b). The total moles of hydrogen in the feed were changed from 790.6 kmol/h to the stoichiometric value of 144 kmol/h.

The results obtained were  $N = 128.8$  kmol/h, Equilibrium Conversion = 0.894 (89.4%).



# Conclusions

- $T < 40^{\circ}\text{C}$  – Refrigeration
- $T > 250^{\circ}\text{C}$  – Fired Heater or Furnace
- $T > 400^{\circ}\text{C}$  – M.O.C. Issues
- $P < 1 \text{ atm}$  – Vacuum and Large Equipment
- $P > 10 \text{ atm}$  – Cost ↑





## SUMMARY

